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RE: Japanes Laid-Open Publicati n N . 1-282291
US Patent No. 5 128 587

(Translation)

Japanese Laid-Open Publication No. 1-282291

Laid-Open Publication Date: November 14, 1989
Application Number: 63-109898
Filing Date: May 7, 1988
Inventor: C. HOSOKAWA
Applicant: IDEMITSU KOSAN KABUSHIKI KAISHA

SPECIFICATION

1. Title of the Invention
Thin-film EL element

2. Claim
A thin-film EL element including an electrode, a hole injection layer, a light emitting layer, and an electrode, wherein a rare earth complex is used as a light emitting material of the light emitting layer.

3. Detailed Description of the Invention
[Field of the Invention]
The present invention relates to a thin-film EL (electroluminescence) element having a hole injection layer and a light emitting layer, which provides high luminance and clear color light emission at a low applied voltage.

[Prior Art and Problems to be Solved by the Invention]
An EL element has features of a high visual recognizability due to a self-light emission system and a superior resistance against impact because of being completely solid-state. Currently, EL elements using ZnS:Mn, which is an inorganic flu rescent material, are widely used. However, such an inorganic EL elem nt r quir s an applied voltage of

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as high as close to 200 V to cause light emission, and thus requires a complicated driving method.

Organic thin-film EL elements can significantly reduce an applied voltage and thus have been developed with various materials. Vincette et al. have already produced an EL element using anthracene as a luminophor and a vapor-deposited film having a thickness of about 0.6 μm, which provides blue light visible in a bright place at an applied voltage of 30 V (Thin Solid Films, 94 (1982) 171). However, this EL element has problems of an insufficient luminance of emitted light and of a high applied voltage still being required.

Recently, an organic EL element emitting light having a luminance of 5 to 90 cd/m^2 at an applied voltage of as low as about 10 V has been produced with a thin film using the LB method (Langmuir Blodget Method) (for example, Japanese Laid-Open Publication No. 61-43682). However, in the case of this organic EL element, laminated layers are produced of a light emitting material capable of accepting electrons and supplying electrons by accumulation of monolayers by the LB method. Therefore, this organic EL element has problems of a complicated structure and troublesome production, and thus is not suitable for practical use.

In order to solve these problems, lamination-type EL elements including electrode/hole injection layer/light emitting layer/electrode, which have a simple structure and emits light of a high luminance at a low applied voltage of 25 V or less, have been developed. These EL elements are disclosed in Japanese Laid-Open Publication No. 59-194393 and Appl. Phys. Lett. 51(12), 21 Sept. 1987. Among these EL elements, an EL lement described in Appl. Phys. Lett. 51(12), which uses an aluminum complex of 8-hydroxyquinoline as a light emitting material and a diamin -based compound as

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a hole injection material, is a superior element providing a luminance of 1000 cd/m^2 at an applied voltage of 10 V or less.

However, these lamination-type thin-film EL elements including electrode/hole injection layer/light emitting layer/electrode have a broad light emitting spectrum, and therefore are inferior in the clearness of colors. Thus, these thin-film EL elements have a problem in that it is difficult to accurately represent each of the RGB colors, i.e., blue, green and red. In the case of the thin-film EL element described in Japanese Laid-Open Publication No. 59-194393, the thickness of the film between the electrodes needs to be 1 μm or less. Therefore, especially when having a large area, this EL element has a problem in that pinholes are easily generated and the productivity is low.

An EL element which has a two-film light emitting layer and uses a rare earth complex or the like as a light emitting organic compound and thus provides light emission having a sufficiently high luminance even at a low voltage has been developed (for example, Japanese Laid-Open Publication No. 61-37887). However, this thin-film EL element is not of a lamination-type including electrode/hole injection layer/light emitting layer/electrode layers. Nor is it disclosed how the brightness, i.e., clearness, of color of the light emitted by the element is improved when a rare earth complex is used as the light emitting material in such a lamination-type EL element.

The present invention, made in light of the above-described circumstances, has an objective of providing a lamination-type thin-film EL element including a hole injecti n layer and a light emitting layer for emitting cl ar

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color light having a high luminance and a sharp spectrum through an application of a low voltage.

[Means for Solving the Problems]

As a result of active studies in order to achieve the objective, the present inventor found that use of a rare earth complex, especially, a fluorescent rare earth complex as a light emitting material of a lamination-type EL element having an electrode, a hole injection layer, a light emitting layer and an electrode, greatly influences the brightness of color of light emitted by the element, and completed the present invention. In other words, a thin-film EL element according to the present invention includes an electrode, a hole injection layer, a light emitting layer, and an electrode, wherein a rare earth complex is used as a light emitting material of the light emitting layer.

Hereinafter, the present invention will be described in detail.

The thin-film EL element according to the present invention is usable both for AC driving and DC driving. In the following description, DC driving will be used with reference to Figure 1.

In Figure 1, reference numeral 1 represents a substrate, which is formed of, for example, glass, plastics or quartz. Reference numerals 2 and 3 represent electrodes interposing a hole injection layer 4 and a light emitting layer 5. One of the electrodes (electrode 2) is formed on the substrate 1 and is formed of, for example, ITO (indium tin oxide), SnO_2 (tin oxide (IV) or ZnO (zinc oxide) to be transparent or semitransparent. The electrode 2 usually has a thickness of 50 nm to 1 μm and pref rably has a thickness of 50 to 200 nm from the point of view of transparency. The other l etrod

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(electrode 3) acts as a counter electrode and is formed of metal such as, for example, gold, aluminum, magnesium or indium. The counter electrode 3 usually has a thickness of 50 to 200 nm.

Depending on the type of the thin-film EL element, the electrode 2 on the substrate 1 may act as a metal counter electrode and the other electrode 3 may act as a transparent or semitransparent electrode.

The hole injection layer 4 is formed of a material which is formed of a hole transmitting compound and has a function of transmitting holes injected from the electrode (positive electrode) 2 to the light emitting layer. A preferable example of the hole transmitting compound has a hole transfer coefficient of at least 10^{-4} cm^2/V-sec when the layer is provided between electrodes supplied with an electric field of 10^4 to 10^5 volts/cm. Especially preferable examples of the hole transmitting compound are aromatic amine compounds.

Preferable examples of the hole transmitting compound include amine compounds which are solid at room temperature and have at least one nitrogen atom tri-substituted with a substituent. In this case, at least one of the tri-substituted groups is an aryl group or a substituted aryl group.

Examples of useful substituents in the aryl group include alkyl groups having 1 to 5 carbon atoms, for example, methyl groups, ethyl groups, propyl groups, butyl groups, and amyl groups; halogen atoms, for example, chlorine atoms and fluorin atoms; and alkoxy groups having 1 to 5 carbon atoms, for example, methoxy groups, ethoxy groups, propoxy groups, butyl groups and amyl groups.

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According to the present invention, the hole transmitting compound needs to be formed into a thin film. Hole transmitting compounds formed into a thin film include a compound expressed by the following formula.

Formula

In the above formula, Q^1 and Q^2 represent groups independently containing a nitrogen atom and at least three carbon cycles (at least one of which is aromatic, for example, a phenyl group). The carbon cycles can each be a saturated cycle, for example, a cyclohexyl group or a cycloheptyl group.

G represents a bonded group, for example, a cycloalkylene group (for example, a cyclohexylene group); an arylene group, for example, a phenylene group; an alkylene group, for example, a propylene group; or a C-C bond. Each of the compounds having the above-shown formula specifically includes the following:

1,1-bis(4-di-p-tolylaminophenyl)-4-phenyl-cyclohexane having the following formula (formula 1):

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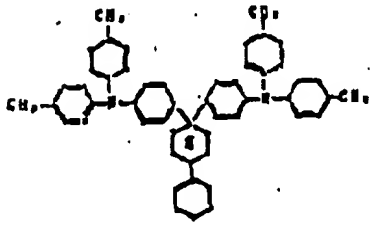
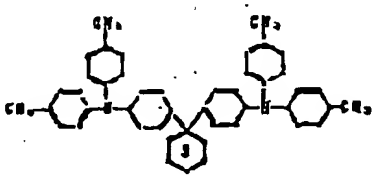
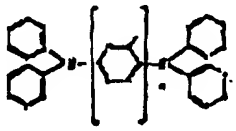


1,1-bis(4-di-p-tolylaminophenyl) cyclohexane having the following formula (formula ii):



iii) 1,1-bis(4-di-p-tolylaminophenyl) cyclohexane and a compound having the following formula (formula iii):



(In the above formulas, n is an integer of 2 to 4.) The compounds expressed by the above formula include, for example, 4,4-bis(diphenylamino) quadriphenyl.

For example, 4,4-bis(4-dimethylamino-2-methylphenyl) phenylmethane and N,N,N-tri(p-tolyl) amine are included.

As the light emitting material of the light emitting layer 5, a rare earth complex is used. Any rare earth com-

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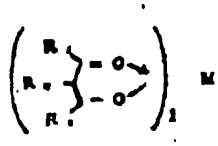
plex is usable, but fluorescent rare earth complexes are preferable from the point of view of the light emission efficiency of the EL element, especially the following rare earth complexes are preferable.

①



R_1 and R_2 are independently:

an alkyl group having a carbon number of 1 to 15, for example, a methyl group, an ethyl group, a propyl group, a butyl group, an i-propyl group, a t-butyl group, an i-butyl group, an s-butyl group, an octyl group, or a nonyl group;

a halogenated alkyl group having a carbon number of 1 to 15 (here, "halogen" refers to chloride, fluorine, bromide or the like), for example, a trifluoromethyl group, a heptafluoropropyl group, a trichloromethyl group, a tribromomethyl group, a dichloromethyl group, a chloromethyl group, a difluoromethyl group, a fluoromethyl group, a dibromomethyl group, or a bromomethyl group;

an aryl group having 6 to 14 carbon atoms, for example, a phenyl group, a naphtyl group, a tolyl group, a xylyl group, or an anthryl group; or

a hetero atom, for example, a 5- or 6-member heterocyclic group containing one nitrogen, oxygen or sulfur atom, for example, a pyrrolyl group, a furyl group, a thienyl group, or pyridyl group.

R_3 is hydrogen or the same as group R_1.

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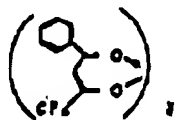
M is a rare earth element. Rare earth elements include, for example, Ce (cerium), Tb (terbium), Sm (samarium), Eu (europium), Ho (holmium), Pr (praseodymium), Gd (gadolinium), Er (erbium), and Tm (thulium).

Rare earth complexes usable in this example include, for example, [Eu(BFA)$_3$] consisting of Eu and BFA (benzoyltrifluoroacetone).

This is expressed by the following formula.



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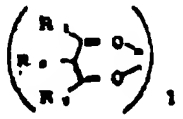

R_1, R_2, R_3 and M have the same definitions as above. "TOPO" is tri-n-octyl phosphine oxide.

Rare earth complexes usable in this example include, for example, [Tb(TTA)$_3$(TOPO)$_2$] consisting of Tb, TTA (thenoyltrifluoroacetone) and TOPO (tri-n-octyl phosphine oxide).

This is expressed by the following formula.

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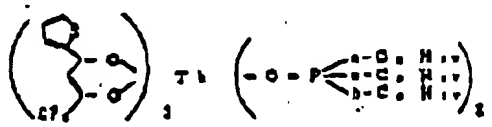
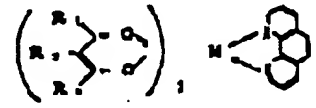
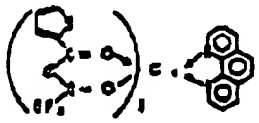


③ 

R_1, R_2, R_3 and M have the same definitions as above.

Rare earth complexes usable in this example include, for example, [Eu(TTA)$_3$(Phen)] consisting of Eu, TTA and Phen (phenanthrolin), [Sm(NTFA)$_3$(Phen)] consisting of Sm, NTFA (2-naphthoylfluoroacetone) and Phen, and [Ce(TTA)$_3$(Phen)] consisting of Ce, TTA and Phen.

[Ce(TTA)$_3$(Phen)] is expressed by the following formula.



Specific examples of the rare earth compounds expressed by formulas ① through ③ are expressed by formulas (1-1) through (6-6).

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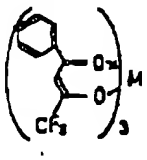
(1-1)[M(BFA)$_3$]



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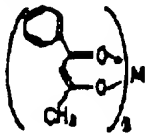

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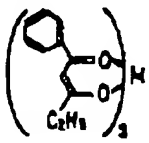

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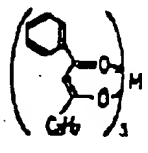

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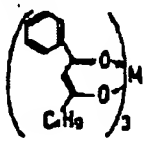

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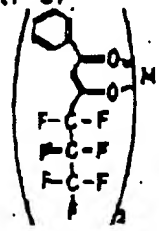

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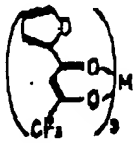

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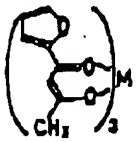

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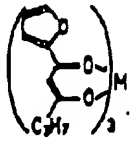

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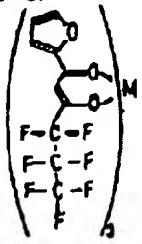
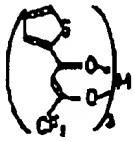


(3-1)[M(TTA)$_3$]



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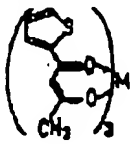

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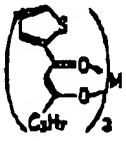

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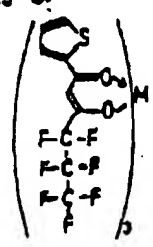

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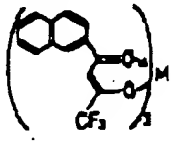

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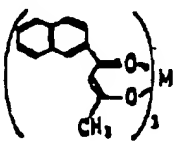

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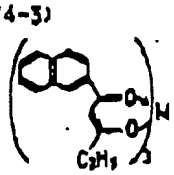

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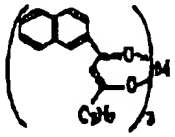

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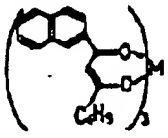

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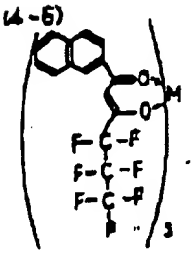

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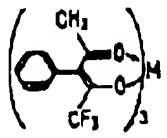

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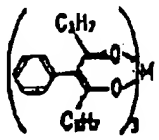
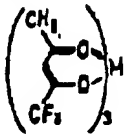


(6-1)



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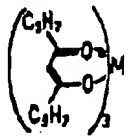
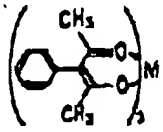


(5-2)



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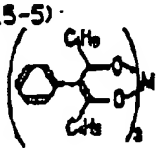

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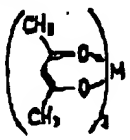

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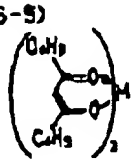
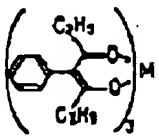
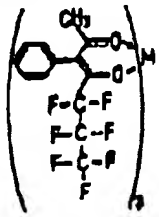


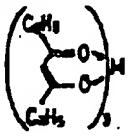
(5-3)



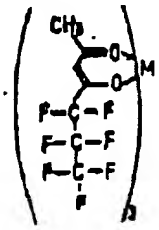
(5-6)



(6-3)



(6-6)



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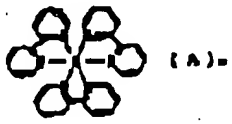
M represents a rare earth element. 1,10-phenanthroline or triooty1 phosphine oxide can be added to formulas (1-1) through (6-6).

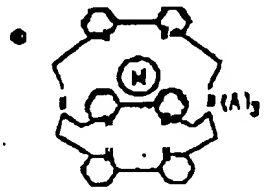
Other preferable examples of the rare earth complexes include:

tris-bi-pyridine rare earth complex salts expressed by the following formula:



where M is a rare earth tervalent ion, and A is an anion, for example, a perchlorate ion, a phosphorus hexafluoride ion, a borofluoride ion, an iodine ion, a bromine ion, a chlorine ion or an acetic acid ion;

rare earth compounds expressed by the following formula:



where M is a rare earth tervalent ion, for example, a terbium ion, and A is an anion which is similar to those listed regarding ④;

bis-pyridine rare earth complex salts expressed by the following formula:

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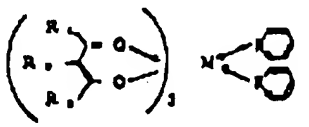
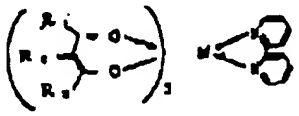


where M is a rare earth tervalent ion; and

bi-pyridine rare earth complex salts expressed by the following formula:



where M is a rare earth tervalent ion.

A thin-film EL element having the above-described structure is produced in the following manner.

First, the transparent electrode 2 is formed on the substrate 1 by vapor deposition, sputtering or the like. Next, a hole transmitting compound is formed into a thin film, thereby providing the hole injection layer 4 on a top surface of the transparent electrode 2. The hole transmitting compound is formed into the thin film by vapor deposition under the following conditions.

(Vapor deposition conditions)

Boat heating condition: 50 to 400°C
Vacuum degree: 10^{-5} to 10^{-3} Pa
Vapor deposition rate: 0.1 to 50 nm/sec.
Substrate temperature: -50 to 200°C
Film thickness: 100 nm to 5 μm

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Then, a light emitting material is formed into a thin film, thereby providing a light emitting layer 5 on a top surface of the hole injection layer 4. The light emitting material is formed into the thin film by spin-coating, casting, LB, vapor deposition or the like. From the point of view of the uniformity of the film, elimination of pinholes and the like, vapor deposition is preferable.

The hole injection layer 4 and the light emitting layer 5 can be performed in the opposite order; i.e., the light emitting layer 5 and then the hole injection layer 4 can be formed, both by vapor deposition. The thin-film EL element formed in this manner has a lamination structure including electrode 2/light emitting layer 5/hole injection layer 4/electrode 3.

Then, the counter electrode 3 of a thin film is formed on a top surface of the light emitting layer 5 or the hole injection layer 4 by vapor deposition, sputtering or the like.

(Example 1)

On a glass substrate having a size of 25 mm × 75 mm × 1.1 mm, ITO was formed to a thickness of 50 nm by vapor deposition. The resultant laminate was used as a transparent support substrate. The transparent support substrate was secured to a substrate holder of a vapor deposition apparatus (ULVAC Japan Ltd.). To a resistive heating boat formed of molybdenum, 200 mg of [Eu(TTA)$_3$(Phen)] was placed. To another boat, N,N,N',N'-tetraphenyl-(1,1'-biphenyl)4,4'-diamine(TPD) was placed. The pressure in the vacuum tank was reduced to 1×10^{-4} Pa.

[Eu(TTA)$_3$(Phen)] was obtained as follows. An queous solution of uropium chloride was adjusted to a pH of 5.5.

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The resultant solution, TTA, and Phen dissolved in a 1:1 mixed solution of acetone and benzene were mixed and extracted. The solvent was removed under a low pressure to obtain [Eu(TTA)$_3$(Phen)]. The obtained [Eu(TTA)$_3$(Phen)] was purified.

The resistive heating boat was heated to 140°C. The above-mentioned complex was vapor-deposited on the transparent support substrate at a vapor deposition rate of 1.0 nm/sec. Thus, a luminophor thin film having a thickness of 1.0 μm was obtained. At this point, the substrate temperature was room temperature.

Another boat was heated to 210°C. TPD was vapor-deposited at a vapor deposition rate of 1.0 nm/sec. A hole injection layer having a thickness of 500 nm was formed on the luminophor thin film. At this point, the substrate temperature was room temperature.

The obtained laminate was removed from the vacuum tank, a stainless steel mask was put on the thin film and secured again to the substrate holder. To the resistive heating boat of molybdenum, 20 mg of gold was placed. The pressure in the vacuum tank was reduced to 2×10^{-4} Pa. The boat was heated to 1400°C, and a gold electrode having a thickness of 100 nm was formed on the luminophor thin film to act as a counter electrode. The element was supplied with a DC voltage of 22 V, using the gold electrode as a positive electrode and the ITO electrode as a negative electrode. As a result, a current of 1.5 mA flowed, and emission of red light was provided.

At this point, the light emission maximal wavelength was 618 nm and the light emissi n luminance was 436 cd/m^2.

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CIE chromaticity coordinates were x=0.65, y=0.34, which indicates clear red.

(Example 2)

An EL element was produced in the same manner as that of Example 1, except that [Sm(NFTA)$_3$(Phen)] was used.

[Sm(NFTA)$_3$(Phen)] was obtained as follows. An aqueous solution of samarium chloride was adjusted to a pH of 5.5. The resultant solution, NFTA, and Phen dissolved in a cyclohexane solution were mixed and extracted. The solvent was removed under a low pressure to obtain [Sm(NFTA)$_3$(Phen)]. The obtained [Sm(NFTA)$_3$(Phen)] was purified.

The boat was heated to 160°C while vapor deposition was performed. The element was supplied with a DC voltage of 31 V. As a result, a current of 25 mA flowed, and emission of red light was provided.

At this point, the light emission maximal wavelength was 654 nm and the light emission luminance was 200 cd/m^2. CIE chromaticity coordinates were x=0.56, y=0.323, which indicates clear red.

(Example 3)

An EL element was produced in the same manner as that of Example 1, except that [Tb(TTA)$_3$(TOPO)$_2$] was used.

[Tb(TTA)$_3$(TOPO)$_2$] was obtained as follows. An aqueous solution of terbium chloride was adjusted to a pH of 4.5. The resultant solution, 2 x 10^{-4} mol/liter of TOPO, and 5 x 10^{-4} mol/liter of hexane solution of TTA were mixed and extracted. Th solvent was removed under a low pressure to obtain [Tb(TTA)$_3$(TOPO)$_2$]. Th obtain d [Tb(TTA)$_3$(TOPO)$_2$] was purified.

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The boat was heated to 140°C while vapor deposition was performed, thereby forming a luminophor thin film having a thickness of 700 nm. The element was supplied with a DC voltage of 13 V. As a result, a current of 1.5 mA flowed, and emission of yellowish green light was provided. At this point, the light emission maximal wavelength was 545 nm and the light emission luminance was 985 cd/m^2. CIE chromaticity coordinates were x=0.34, y=0.56, which indicates clear yellowish green.

(Example 4)

An EL element was produced in the same manner as that of Example 1, except that [Ce(TTA,)Phen] was used.

[Ce(TTA),Phen] was obtained as follows. An aqueous solution of cerium chloride was adjusted to a pH of 4.5. The resultant solution, TTA, and Phen dissolved in a 1:1 mixed solution of acetone and benzene were mixed and extracted. The solvent was removed under a low pressure to obtain [Ce(TTA),Phen]. The obtained [Ce(TTA),Phen] was purified.

The boat was heated to 145°C while vapor deposition was performed, thereby forming a luminophor thin film having a thickness of 600 nm. The element was supplied with a DC voltage of 34 V. As a result, a current of 40 mA flowed, and emission of bluish purple light was provided.

At this point, the light emission maximal wavelength was 400 nm and the light emission luminance was 180 cd/m^2. CIE chromaticity coordinates were x=0.17, y=0.02, which indicates clear bluish purple.

As a result, it was found that a thin-film EL according to the present invention including a hole injection layer

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and a light emitting layer emits light the RGB colors, i.e., blue, green and red, with a high luminance, a sharp spectrum and a high color saturation by an application of a low voltage. This has realized color displays or the like consisting of a thin-film EL element emitting light of various colors with a high clearness. It was also found that the thin-film EL according to the present invention is easily produced at a high productivity.

[Effect of the Invention]

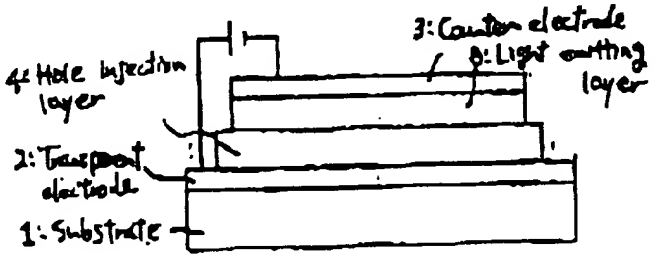
As described above, a thin-film EL element according to the present invention provides an effect of emitting light having a high luminance and a clear color.

4. Brief Description of the Drawings

Figure 1 is a schematic structural view illustrating one example of a thin-film EL element according to the present invention of a DC driving type.

1: substrate; 2: transparent electrode; 3: counter electrode; 4: hole injection layer; 5: light emitting layer

Fig. 1



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Amendments

June 28, 1989

To Mr. Fumitake YOSHIDA, Commissioner of the Patent Office

1. Identification of the Case
Japanese Application No. 63-109898

2. Title of the Invention
Thin-film EL element

3. Party who files the Amendments
Relationship with the case: Applicant

Address: 3-1-1, Marunouchi, Chiyoda-ku, Tokyo
Name: Idemitsu Kosan Kabushiki Kaisha

4. Agent Phone: 5256-6866
Address: Kanda Araki Bldg., 5th Fl.
1-14-6, Kanda-suda-cho, Chiyoda-ku, Tokyo
Name: (8675) Kihei WATANABE, Patent Attorney

5. Date of instruction to amend: preliminary amendment

6. Item to be amended: Specification

7. Amendments

*Translation note: The following page and line numbers are in the English translation.

(1) Specification, page 3, 1st full paragraph, lines 7 to 12: "In the cae ... is low." is deleted.

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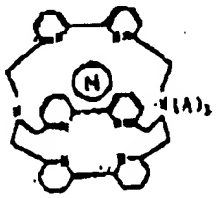
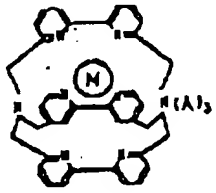
(2) Specification, page 3, 2nd full paragraph, line 1: a typographical error in Japanese regarding "two-film" is corrected.

(3) Specification, page 13, 2nd formula (formula ⑤):



is corrected to:



(4) Specification, page 13, 5th line from the bottom and page 14, 1st line below 1st formula: "rare earth tervalent ion" is corrected to "rare earth element".

(5) Specification, page 14, last line: "100 nm" is corrected to "100 Å".

(6) Specification, page 15, 4th line from the bottom: a typographical error regarding "(TPD)" is corrected.

(7) Specification, page 16, 1st full paragraph, line 4 and 2nd full paragraph, line 2: "1.0 nm/sec" is corrected to "1.0 Å/sec".

(8) Specification, page 16, 1st full paragraph, line 5: "1.0 μm" is corrected to "1000 Å".

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(9) Specification, page 16, 2nd full paragraph, line 3: "500 nm" is corrected to "500 Å".

(10) Specification, page 16, 3rd full paragraph, line 4: "20 mg of gold" is corrected to "2 g of gold".

(11) Specification, page 18, line 3: "700 nm" is corrected to "700 Å".

(12) Specification, page 18, 4th paragraph, line 3: "600 nm" is corrected to "600 Å".

(13) Specification, page 18, between 3rd line from the bottom and 2nd line from the bottom, the following paragraphs are inserted.

"(Example 5)

A glass substrate (size: 25 mm x 75 mm x 1.1 mm; HOYA) provided with an ITO layer having a thickness of 100 nm to be used as a transparent electrode was used as a transparent support substrate. The transparent support substrate was treated with ultrasonic washing with isopropyl alcohol for 30 minutes and then immersed in isopropyl alcohol for further washing. The resultant transparent support substrate was dried with drying nitrogen gas and secured to a substrate holder of a commercially available vapor deposition apparatus. To a resistive heating boat formed of molybdenum, 200 mg of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPDA) was placed. To another resistive heating boat of polybutene, 200 mg of [Eu(TTA)$_3$(Phen)] was placed, and the resistive heating boat was set in the vapor deposition apparatus. Then, The pressur in the vacuum tank was reduced to 3 x 10^{-4} Pa. The boat containing TPDA was supplied with electric power s as to be